Biomedically Relevant Chemical and Physical Properties of Coal Combustion Products

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The evaluation of the potential public and occupational health hazards of developing and existing combustion processes requires a detailed understanding of the physical and chemical properties of effluents available for human and environmental exposures. These processes produce complex mixtures of gases and aerosols which may interact synergistically or antagonistically with biological systems. Because of the physicochemical complexity of the effluents, the biomedically relevant properties of these materials must be carefully assessed. Subsequent to release from combustion sources, environmental interactions further complicate assessment of the toxicity of combustion products. This report provides an overview of the biomedically relevant physical and chemical properties of coal fly ash. Coal fly ash is presented as a model complex mixture for health and safety evaluation of combustion processes.

Source Term

Coal fly ash is the particulate matter remaining after combustion of the carbonaceous component of coal. The residual, accessory minerals, predominately clay and siliceous minerals, generally comprise the bulk of the ash. It has been estimated that the United States will burn up to 850 million tons of coal in 1985 (1), of which approximately 11% is ash. Of the total ash, 80% is fly ash (i.e., ash that leaves the combustion zone of the power plant boiler) and 1-5% is released to the atmosphere (1). Thus, one may calculate that approximately 100 million tons of fly ash will be produced in the U.S. in 1985. Interestingly, in 1977, fly ash was considered to be the sixth most abundant mineral in the U.S. (2).

Although a number of uses for fly ash have been discussed, less than 20% is reused commercially in the U.S., predominantly in cement or as a fill material in construction (2). Efforts to utilize fly ash as a soil amendment for either pH control or trace element supplementation have been thwarted by the presence of relatively toxic minerals and/or

mutagenic components. The economic feasibility of aluminum recovery from fly ash is presently under evaluation (3). Most of the fly ash collected in power plants is disposed by deposition in landfills.

General population exposure results from the release of fly ash from the stack of the power plant. Although all modern power plants in the U.S. utilize particle abatement technology, a substantial mass of ash escapes the control devices. Control is generally effected by use of an electrostatic precipitator (ESP) alone or in combination with a Venturi wet scrubber. More recently, baghouse filtration is under evaluation for particulate abatement. Because the ESP is least efficient for collection of the finest fly ash particles (4), the size distribution of aerosols from coal combustion is generally in the respirable mode.

Most studies of the physical properties and toxicological activity of fly ash have been directed at the readily available ESP-collected material. This material may not be an appropriate surrogate, because after release of fly ash to the atomsphere, environmental interactions will alter physical and chemical properties. However, collection of sufficient quantities of ambient fly ash from plumes for detailed physical characterization and biological evaluation is presently not feasible.

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Fly Ash Collection

Collection of representative samples of coal fly ash for health assessment has been elusive and oftentimes fraught with technical difficulties. As previously described, most studies have utilized readily available ESP ash. ESP sampling generally is associated with two primary deficiencies: sample inhomogeneity and lack of correlation with stack-released material.

Sample inhomogeneity is the result of inherent differences in the parent coal, engineering design, and varying combustion and collection conditions within an individual power plant. It is well known that the combustion conditions and particle control systems may vary substantially throughout the operation of a single power plant. Furthermore, differences in coal types, even from the same mines, may dramatically alter the ash combustion. Also, although hundreds of kilograms of ESP ash may be readily sampled from a power plant, this mass may represent less than 0.1% of the daily ash generation. Thus, even for evaluation of the occupational hazards of inplant fly ash, extreme care must be taken to sample an appropriate homogenate of ash for subsequent analysis.

Most concern, however, is focused on the estimation of the potential public health impact of coal combustion. In this regard, it is well documented that the physical and chemical properties and biological activity of fly ash are functions of the history of the particles. This review will emphasize differences in material collected from the ESP, the smokestack, and the emitted plume.

Design of stack and plume sampling technologies requires careful consideration of the expected application of the data. Because many of the properties of fly ash depend on the particle size (5), *in situ* classification procedures are often utilized. The mass requirement usually determines the appropriateness of the sampling methodology. While morphological analysis may be performed by electron or light microscopy on microgram quantities, elemental analysis generally requires milligram quantities and chemical analysis usually requires more than 1 g. Similarly, biological testing using *in vitro* techniques may require 0.01–0.1 g quantities for macrophage assays and 0.1–1 g quantities for mutagenicity evaluation. Acute inhalation studies may be performed with 10-100 g quantities, while chronic inhalation studies require 100 kg of size-classified particulate matter. Thus, sampling strategies may vary greatly depending on the ultimate study goals.

Stack and plume sampling of fly ash for subsequent analysis is often accomplished using glass fiber filters. This methodology does not permit size classification for subsequent chemical and biological study. Furthermore, artifactual changes in the fly ash composition may result from the continued exposure of collected material to the effluent flue stream (6). Most efforts are presently directed at collection of size-classified material. Stack collection of size-classified material normally involves isokinetic sampling using the principle of inertial impaction. Such devices often involve a cascade of acceleration nozzles and impaction plates to continuously classify finer and finer particles. Cascade impactors are limited to collection of less than 100 mg of size-classified material. Furthermore, because they are operated over relatively short time periods (less than 1 hr), fluctuations due to varying plant operating condition may go undetected. To collect kilogram quantities of stack fly ash, McFarland et al. (7) used a specially designed fractionator consisting of two cyclone separators and a centripeter employing multiple jets. The separation devices were maintained at constant temperature in a heated, insulated enclosure. The collected material was cleaned at 2-min intervals from the fabric filters to avoid substantial pressure drops. This procedure also minimized extensive exposure of filter-collected material to the flue stream. It should also be pointed out that the sampling system was operated continuously over a 30-day period. Thus, this approach may provide a representative sample reflecting variations in plant operating conditions throughout the relatively long sampling period. Further development is needed, however, in the collection of representative stack fly ash samples for toxicological evaluation.

Plume sampling presents further technical difficulty in ash collection. Because ESP collection of particles is least efficient for the finest particle and the sedimentation velocities of large, nonrespirable particles are greater than those of particles in the respirable mode, collection of respirable plume samples does not require size classification. Plume tracking and measurement of dynamic changes in composition are usually accomplished by airplane, helicopter or tethered balloon sampling. Collection of masses greater than 100 mg is generally not possible. Occasionally, because of a unique combination of geographical and meteorological conditions, plumes may be sampled at their site of "touch-down." Such sampling is presently underway in California and Utah (D. Eatough and L. Hansen, personal communication). The touch-down sites generally use high-volume samplers that may employ aerodynamic impaction, filteration and/or electrostatic precipitation, alone or in combination. This approach may have daily yields of gram quantities of fly ash. However, alterations in meteorological conditions and the contribution of other

environmental aerosols, both anthropogenic and natural, may cloud the evaluation and interpretation of data from these samples.

It is important that the limitations in sample collection be considered in interpretation of the physical and chemical data describing fly ash and in the extrapolation of biological testing to the estimation of human health impacts.

Physical Characterization

Morphology

The morphology of fly ash has been the subject of numerous reports. Fly ash morphogenesis is the result of the initial mineral composition of the coal and the subsequent time-temperature history occurring in the combustion zone of the boiler (8,9). Light microscopic evaluation of fly ash (10) indicates a vast array of morphological forms and colorations. One study (11) classified the relative abundances of 11 morphological classes: amorphous, nonopaque particles; amorphous, opaque particles; amorphous, mixed opaque and nonopaque particles; rounded, vesicular, nonopaque particles; rounded, vesicular, mixed opaque and nonopaque particles, angular, lacy, opaque particles; cenospheres or hollow spheres; plerospheres or encapsulating spheres; nonopaque solid spheres; opaque spheres; and spheres with either surface or internal crystals. A morphogenesis scheme has been developed relating the 11 morphological classes to extent and duration of exposure to combustion zone temperatures and probable matrix composition. Opaque amorphous particles and angular, lacy, opaque particles were tentatively classified as unoxidized carbonaceous material or iron oxides (9). Subsequent scanning electron microscopy–x-ray analysis (SEM) (10,11) indicated that these opaque nonspherical particles were composed of low atomic number matrices predominantly elemental carbon. The opaque shperes appeared to be predominantly magnetite and could be identified by magnetic separation or by observation of small homogeneous clusters of these particles. The amorphous and rounded vesicular, nonopaque particles appear to be aluminosilicate particles. Further heating of these particles may give rise to nonopaque spheres that are either solid, hollow, or packed with other particles. Similarly, the mixed opaque, nonopaque, amorphous, or rounded classes will give rise to spherical particles upon increased exposure to combustion conditions in the boiler. The nonopaque, solid spheres ranged in color from water white to deep red. Crystals within glassy spheres are probably formed by heterogeneous nucleation within the molten silicate droplet. In this regard, Gibbon (12) and Hulett et al. (13) have demon-strated the presence of mullite crystals within and on the surface of fly ash particles. Crystal formation within glassy spheres was demonstrated by transmission electron microscopy (TEM) of hydrofluoric acid-etched replicas. In contrast to the encapsulation of mullite within the glass matrix, it appears that α-quartz particles may be free particles (unpublished data).

The distinction between encapsulated and free crystalline components is of potential health significance. Studies are necessary to evaluate the toxicity of mullite and quartz in fly ash compared to the toxicity of these minerals in the free states. Further justification for mullite and quartz toxicity studies is presented in the chemical analysis section.

Light and electron microscopic studies have identified a morphological class of spherical particles containing encapsulated smaller spheres. These encapsulating spheres or plerospheres (8) are similar to cenospheres, in that they are composed of an aluminosilicate shell but are filled with individual particles rather than gas.

Cenosphere and plerosphere formation probably is the result of similar processes. Raask (14) demonstrated that cenosphere formation may result from melting of mineral inclusions in coal on a nonwetting surface, namely carbon. He also demonstrated that gas generation inside the molten droplet resulted in cenosphere formation. The analysis of major elements in ESP ash indicated that the mass of the cenospheres consisted of 75-90% aluminosilicate, 7-10% iron oxide and 0.2-0.6% calcium oxide. The mass median diameter of the sieved cenospheres from four power plants ranged from 80 to 110 μm. Raask analyzed the gas content of the cenospheres and found approximately 0.2 atm (20°C) of gas composed of CO_2 and N_2. It is hypothesized that the observed CO_2 evolution is due to either carbon oxidation by Fe_2O_3 (14) or carbonate mineral decomposition (8). Assuming a diameter of average volume of 100 μm, a density of 0.5 g/cm^3 and 0.5% CaO content, only 20% of the calcium present in the ash need be associated with carbonate mineral to provide sufficient CO_2.

The mechanism of plerosphere formation has been hypothesized to result from the coexistence of three physical states (8). As the aluminosilicate particle is heated, a molten surface layer develops around the solid core. Evolution of CO_2 and H_2O results in formation of a bubble around the core, which remains attached to the molten shell. Further heating leads to additional gas formation causing the core to boil away from the shell. Concomitant formation of fine particles may result from internal and external busting processes. This process can be repeated until the plerosphere is full of other plerospheres or solid particles or until the particle freezes. The

characteristic time for formation of a 50-μm diameter plerosphere was calculated to be about 1 msec.

Surface crystals identified by SEM have been explained by reaction of sulfuric acid with metal oxides. This crystal formation process is relatively slow compared to the time required for particle formation. Fisher et al. (8) have hypothesized that surface crystal formation results from SO_2 hydration and subsequent oxidation on fly ash surfaces to form H_2SO_4, which then reacts with metal oxides, predominantly CaO, or with ambient NH_3 to form either $CaSO_4$ or $(NH_4)_2SO_4$. Such a mechanism could also result in formation of soluble compounds from relatively insoluble oxides, e.g., conversion of PbO to $PbSO_4$. Thus, interaction of refractory metal oxides with surface sulfuric acid may result in increased bioavailability of biologically active trace elements.

The relative abundances of the 11 light microscopically defined morphological classes in four size-classified, stack-collected fly ash fractions have been quantified (9). The four fractions had volume median diameters (VMD) of 2.2, 3.2, 6.3, and 20 μm with associated geometric standard deviations (σ_g) of approximately 1.8. Only the nonopaque solid spheres increased in abundance with decreasing particle size; all other morphological classes appeared to increase in frequency with increasing particle size. Amorphous and vesicular particles predominated in the coarsest fraction (66% by number). The vast majority of amorphous and vesicular particles were cenospheres; plerospheres never exceeded 0.5% in abundance.

It is interesting to note that the average particle densities of the four fractions correlated directly with the abundance of solid, nonopaque spheres and inversely with cenospheres. Thus, the inverse dependence of density with particle size can be explained on the basis of particle morphology. Because of the predominance of solid, nonopaque spheres in the respirable mode, environmental distribution and public exposure to fly ash may be modeled assuming solid, spherical particles generally with densities approaching that of clay minerals, i.e., 2.5 g/cm³.

Size Distribution

The particle size distribution of fly ash is the result of a number of interacting factors: the initial size distribution of the coal particles, the size-distribution of the accessory minerals, the power plant combustion conditions and the particulate abatement technologies. Unfortunately, the relative importance of these interacting factors is not well defined. From a human health perspective, initial concern is centered on the aerodynamic particle size because it is the aerodynamic behavior that determines environmental transport and respiratory tract deposition. Recently, the ad hoc working group of the International Standards Organization (15) has made recommendations defining particle size ranges in ambient sampling for health effect assessment.

The group points out that soluble particles or droplets may be absorbed at their site of deposition. Other particles may impact differently depending on the specific anatomic region of deposition and the biological reactivity of the individual particle. Particles depositing extrathoracically or depositing in the tracheobronchial region will be swallowed after clearance and may cause their effects directly on the gastrointestinal tract or, if absorbed, may induce systemic effects. Particles depositing in the alveolar region are cleared very slowly (100 days) by solubilization, mucociliary transport, or through the lymphatic system (16). The working group recommended division of the particle size region into three fractions: inspirable (fraction drawn into nose or mouth), extrathoracic (fraction of inspirable not passing the larynx) and thoracic (fraction depositing into the tracheobronchial and alveolar regions). They point out that the choice of deposition curves and appropriate sampling technologies depends on mouth versus nose-breathing, the population at risk, and the nature of the particulate matter. Extrathoracic deposition of corrosive or reactive materials may be of major concern, while different concerns may apply to protection against insoluble particles in the "healthy adult" or the "sick and infirm." The maxima in fractional deposition are approximately 30 μm, 8 μm and 2 μm for the extrathoracic, tracheobronchial and alveolar fractions, respectively. Thus, the definition of the thoracic fraction is consistent with the 10 μm cut-size recommendation by the EPA for "inhalable particles." Presently, most sampling technologies are designed to quantify particle size distributions from approximately 15 μm to 0.5 μm.

With regard to factors affecting the particle size distribution of coal ash, Padia et al. (17) and Sarofim et al. (18) studied the behavior of ash in pulverized coal under simulated combustion conditions. Mineral inclusions tend to melt together as the carbon surface of coal recedes during combustion. Thus, the number of ash particles, per coal particle, that coalesce during combustion is a major determinant of the fly ash size distribution. In their study, Sarofim et al. (18) found an average of three to five fly ash particles are produced for each pulverized coal particle which ranged in mass median diameter (MMD) from approximately 40-80 μm. Thus, this process results in formation of particles larger than the 2-μm particles often associated with clay minerals.

As previously stated, combustion conditions may also affect the particle size distribution. Coal combustion in a chain grate stoker, a pulverized coal-fed unit and a cyclone-fixed unit resulted in boiler emissions with mass median diameters of 42, 18 and 6 μm, respectively (16). The particle size of emitted fly ash is dependent on the specific control strategies. Vandegrift et al. (4) described collection efficiency as a function of particle size for a variety of control technologies including electrostatic precipitators, fabric filters, wet scrubbers, and cyclones. Average collection efficiencies for a medium-efficiency ESP were 90, 70 and 35% for 1.0, 0.1 and 0.01 μm particles, respectively. Interestingly, the Venturi wet scrubber (VWS) was more efficient (99.5%) for 1.0 μm particles and less efficient (<1%) for 0.01 μm particles. A crossover in the ESP and VWS efficiency curves was observed at 0.35 μm. McElroy et al. (19) reported that the fabric filter baghouse is approximately 10-fold more efficient than the ESP for ranging from 1.0 to 0.05 μm.

Examination of submicrometer particles indicates that this mode is in excess of the mass expected from the mineral distribution in coal. A number of investigators have commented on the submicron mode and most agree that it is the result of volatilization or decomposition of ash components followed by condensation and coagulation. Also, a "bursting" mechanism driven by gaseous decomposition products may contribute to the submicron mode.

Most recently, McElroy et al. (19) emphasized the importance of the submicrometer mode in the fly ash size distribution. They reported that the particle size distribution at the outlet of six utility boilers peaked at 0.1 μm. The submicrometer mode contained 0.2-2.2% of the total fly ash mass, although for one plant this mode accounted for 20% of the mass of ash emitted from the stack. A correlation of NO and particle mass in the submicrometer mode was observed. Nitric oxide is thought to be an indicator of combustion temperature, which, in a similar fashion, determines extent of mineral decomposition and volatilization. The presence of a relatively large mass (1%) of fly ash in the submicron mode is of particular interest in the evaluation and design of particulate abatement technologies. The potential health impact of the submicron mode will be discussed further after a review of the elemental composition of coal fly ash.

Thus, there are three distinct particle size modes for coal combustion aerosols. The supermicron mode (>5 μm) generally reflects mineral agglomeration; the micron mode (1-2 μm) results from the size distribution of the clay minerals associated with coal; and the submicron mode (<0.5 μm) is the result of both gaseous bursting of aluminosilicate spheres and homogeneous gas-phase nucleation with subsequent agglomeration.

Chemical Characterization

Elemental Analysis

Natusch and his co-workers (20–23) were the first to emphasize the importance of particle size in fly ash analysis. Their work over the years showed preferential concentration of volatile trace elements on fly ash surfaces. Natusch was astute to point out the potential environmental and health hazards of the surface enrichment phenomenon. Surface deposition of trace elements results in increased concentration with decreasing particle size. Therefore, the finest, most respirable particles with the highest probability of escape from coal power plants and the broadest environmental distribution, also have the highest concentrations of biologically active trace elements. In these early studies, the elements showing "pronounced" concentration trends of increased concentration with decreasing particle size were Pb, Tl, Sb, Cd, Se, As, Ni, Cr, Zn and S. Elements classified as showing limited concentration trends were Fe, Mn, V, Si, Mg, C, Be and Al. The elements described as showing no concentration trends were Bi, Sn, Cu, Co, Ti, Ca and K. The mechanism of concentration enhancement was postulated to be volatilization of the element (or compound) at combustion temperatures (1400-1600°C) followed by condensation on particle surfaces. Thus, fine particles with their large ratio of surface area to mass preferentially concentrate volatile chemical species. Also, those elements displaying the greatest concentration dependence with particle size generally are associated with chemical forms that boil or sublime at coal combustion temperatures.

Fisher et al. (24) have described the size dependence of the elemental concentrations in coal fly ash collected from the stack of a power plant burning low-sulfur, high-ash, western United States coal. Elements were classified into two categories: elemental concentrations dependent on particle size and those independent of particle size. In order of decreasing dependence on particle size, the elements Cd, Zn, As, Sb, W, Mo, Ga, Pb, V, U, Cr, Ba, Cu, Be and Mn displayed increased concentration with decreasing particle size. Silicon was the only element to decrease in concentration with decreasing particle size. The elements not displaying clear-cut concentration dependence on particle size were Al, Fe, Ca, Na, K, Ti, Mg, Sr, Ce, La, Rb, Nd, Th, Ni, Sc, Hf, Co, Sm, Dy, Yb, Cs, Ta, Eu and Tb. Coles et al. (25) described elemental behavior of the same fly ash samples in terms of elemental enrichment factors relative to the parent coal. The elements were grouped into three classes: group I elements displayed little or no enrichment in fine particles and were lithophilic; group II elements displayed marked enrichment and were chal-

cophilic (sulfur associated); and group III consisted of elements with behaviors intermediate to groups I and II. Group I elements included Al, Ca, Cs, Fe, Hf, K, Mg, Mn, Na, Rb, Sc, Ta, Th, Ti, Ce, Dy, Eu, La, Nd, Sm, Tb and Yb; group II elements were As, Cd, Ga, Mo, Pb, Sb, Se, W and Zn; and group III consisted of Ba, Be, Co, Cr, Cu, Ni, Sr, U and V. In a separate report, Coles et al. (26) described enrichment factors for ^{228}Th, ^{228}Ra, ^{210}Ra, ^{238}U and ^{235}U, relative to ^{40}K. Although the enrichment of all radionuclides appeared to increase with decreasing particle size, ^{210}Pb, the most volatile radionuclide, showed the greatest size dependence.

The elemental composition of the submicrometer particle-size mode has been the subject of few studies. Ondov et al. (27,28) reported bimodal size distributions for the elements Cr, Sb, As, U, Se and Br in impactor-collected, stack fly ash samples. The bimodal distributions were separated by a broad minimum between 0.5 and 2 μm. Fisher et al. (29) performed filtration studies with neutron-irradiated coal fly ash. A marked enhancement in the concentration of U, Sb, As, Zn, W and Cr was observed in particles passing through membrane filters with average pore size of 0.2 or 0.4 μm. Most recently, McElroy et al. (19) reported on the composition of fine particles from coal combustion. They found, in contrast to Fisher et al. (29) and Ondov et al. (27) that virtually all elements were enhanced in the submicrometer mode. Thus, McElroy et al. suggest that the model of vapor-phase condensation extends to the submicrometer regime, while Fisher et al. and Ondov et al. have reported that the submicrometer elemental enhancement is the result of homogeneous nucleation. It is probable that both mechanisms are acting in concert, resulting in the particle size dependence of fly ash trace elements.

Many other studies have been performed which are also in basic agreement with the hypothesis of Natusch et al.: the most volatile elements (or their oxides), Cd, Zn, Se, As, Sb, W, Mo, Ga, Pb and V, display the greatest size dependence. Furthermore, the least volatile elements do not display a strong particle size dependence. It should be pointed out that some volatile elements such as Hg and Se may be emitted to the atmosphere in the vapor phase, without condensation on fly ash surfaces.

The concentration of trace elements in fly ash can be partitioned between matrix and nonmatrix associations. Matrix elements tend to be those initially adsorbed onto clay minerals or dissolved and entrapped in the aluminosilicate melt. Nonmatrix elements are those that are surface-associated or contained in nonclay mineral matrices. Hansen and Fisher (30) indicated that the total concentration C_T of an element was the sum of the matrix C_M and nonmatrix C_N concentrations:

$$C_T = C_M + C_N \tag{1}$$

By substituting an extracted concentration C_A and assuming a spherical deposition model, they derived the following relationship:

$$C_T = C_M + C_A(6/D_V\rho) \tag{2}$$

where D_V is the diameter of average volume and ρ the particle density. By plotting C_T versus $(6/D_V\rho)$, and extrapolating to infinite diameter, the value of C_M is obtained. Therefore, C_N can be calculated by application of C_N to eq. (1), and the fraction of matrix versus nonmatrix elemental concentration may be derived. This model was verified by dissolution studies using varying concentrations of HF or HCl. The results for the four previously described fly ash samples indicated that greater than 70% of the Ti, Na, K, Mg, Hf, Th and Fe were associated with the aluminosilicate phase. More than 70% of the As, Se, Mo, An, Cd, W, V, U and Sb were associated with the surface of the particles. A separate mineral phase, possibly apatite (31), was suggested for Ca, Sc, Sr, La, the rare earth elements and possibly Ni.

Light and electron microscopic studies have been used to describe the heterogeneity of particles contained in fly ash. As previously indicated (9), examination by light microscopy demonstrated the presence of a variety of particle morphologies and colors. The presence of particles rich in Al, Si, Ca, Fe, Ti and S was reported by Pawley and Fisher (32). Further studies by Hayes et al. (33) demonstrated enhancements of 20- to 30-fold in the individual particle concentrations of P, Mn, Ti, Fe and S compared to the bulk analysis of the fly ash sample.

The chemical heterogeneity of individual fly ash particles has prompted Hayes et al. (34) to propose a model of toxicity of individual lung cells based on the unique elemental composition of single fly ash particles. The authors point out that although bulk elemental analysis accurately reflects the average composition of fly ash, individual particles may present uniquely toxic compositions. Because fly ash particles will be phagocytized by macrophages shortly after deposition in the tracheobronchial region of the respiratory tract, a model of single cell toxicity may be appropriate. Thus, the segregation of elements in specific particles results in the possibility of significantly higher exposure levels to individual cells than those expected by elements in particles uniformly deposited throughout the respiratory tract. Studies of the macrophage toxicity of relatively insoluble metals compared to equivalent concentrations of soluble metals support this hypothesis. In particular, "insoluble" Ni_3S_2 has been shown to be substantially more toxic than soluble $NiCl_2$

with *in vitro* macrophage exposure (unpublished results).

The bioavailability of fly ash trace elements has not been studied in detail. Solubility studies with neutron-activated fly ash at pH 7.3 indicated that the elements Mo, Ca, Se, Ba, Na, Co, B, As, Zn, W and Cr were partially soluble in the buffer (*29*). Greater than 10% of the mass of Mo, Zn, W, Se, Ba and Ca was rapidly dissolved. Further studies are necessary to define *in vivo* the bioavailability of trace elements in coal ash.

In terms of environmental transport, Gutenmann et al. (*35*) have reported that sweet clover grown on a fly ash landfill contained up to 200 ppm selenium. Subsequent studies (*36*) have demonstrated selenium transport from fly ash-amended soil to asters to pollen collected by honeybees from the flowers. Generally, however, trace element leaching resulting from fly ash fallout in the environs of a power plant is not considered an environmental problem.

Inorganic Chemical Forms

Analysis of individual particles by x-ray diffraction has demonstrated the presence of mullite crystals within specific fly ash particles (*12,13*). Quartz particles do not appear to be encapsulated in fly ash particles. The most abundant crystalline components of fly ash are quartz, mullite and magnetic iron oxides (magnetite and γ-Fe_2O_3) (*13,37*). The magnetic component of the ash is significantly enhanced in Cr, Mn, Co and Ni (*37*). The enhancement is thought to be the result of isomorphic substitutions in the magnetic spinel lattice. In ESP ashes from four power plants, Hulett et al. (*13*) report magnetic fractions varying from 17-97% of the total mass. In finer fly ash samples, Hansen et al. (*37*) reported 2% of the mass was magnetically separable. Mullite and quartz contents of ash have been reported (*13,37*) to vary from 2.0-17% and 1.3-14%, respectively. The concentration of crystalline components has been observed to decrease with decreasing particle sizes (*37*). Mullite and magnetic iron oxides are thought to be formed during the combustion process while quartz is probably an accessory mineral present in the coal.

Bauer and Natusch (*38*) described the presence of carbonate compounds in coal fly ash. Total carbonate concentrations were 1% and identified as alkali, alkaline earth and ferrous carbonates. Hansen et al. (unpublished results) studied the chemical speciation of sulfur. Heat treatment of fly ash results in SO_2 evolution, possibly the result of sulfate decomposition and subsequent SO_3 reduction. Only the S(VI) [not S(IV)] species have been identified in the fly ash samples. The sulfate was shown to be surface-associated.

Unfortunately, there exists a dearth of information on the oxidation state and chemical form of the biologically active trace elements. These data are necessary to evaluate the potential bioavailability and toxicity of trace elements in coal fly ash.

Organic Chemical Forms

The organic chemical composition of coal fly ash is poorly described. Only a few studies have been made of the qualitative and quantitative organic composition of coal fly ash. Organic compounds are expected to predominate in the vapor phase throughout the residence period of the fly ash particle in the power plant. Therefore, as postulated by Natusch and Tomkins (*39*), organic compounds are generally present as gases at the temperatures encountered within the power plant, but rapidly adsorb onto fly ash surfaces as the temperature falls either in the smoke stack or as the flue gas stream exits the stack. Support for this hypothesis is derived from theoretical calculations of polycyclic aromatic hydrocarbon (PAH) phase equilibrium, chemical analysis and the biological activity of coal fly ash.

Although a variety of PAHs, including benzo-(a)pyrene, 1,2-benzoanthracene and 20-methylcholanthrene, have been extracted from fly ash, only a few compounds have been quantified (*40*). Tomkins (*41*) demonstrated greater concentrations of polycyclic organic matter (POM) emitted from the stack of a power plant compared to that collected within the stack. While phenanthrene, fluoranthene, pyrene, benzofluorene, methylpyrene, benzophenanthrene and benzo(a)pyrene were not detectable in stack-collected samples, the following concentrations were found in plume samples, 9, 19, 12, 2, 1, 3, and 5 µg/g, respectively. Generally, most studies report the total organic composition of fly ash to be less than 100 µg/g. The emission of POM appears to be dependent on the efficiency of the combustor. PAH emission per unit mass of coal has been reported to be 1000-fold greater for hand-fired furnaces compared to chain grate stokers (*18*). Pulverized coal combustion generally results in less PAH emission than that from the chain grate stokers.

Fly ash surfaces may stabilize adsorbed PAH against photochemical decomposition (*42,43*). In laboratory studies, gas-phase PAHs were passed through a bed of fly ash. Samples were irradiated using outdoor sunlight as well as artificial light sources. In contrast to irradiation in solution where extensive degradation occurred, appreciable photodegradation was not observed for pyrene, phenanthrene, fluoranthrene, anthracene and benzo(a)-pyrene. Anthracene and benzo(a)pyrene adsorbed onto alumina were sensitive to photodecomposition. However, a number of PAHs were shown to oxidize

spontaneously on fly ash surfaces in the absence of light. Most of the compounds that demonstrated spontaneous decomposition contained benzylic carbon atoms (fluorene, benzofluorenes, 9,10-dimethylanthracene, 9-azafluorene) which may be oxidized to form ketones or quinones. Furthermore, studies by Hughes et al. (44) indicated that reaction of surface-associated PAH with SO_3 or NO_2 resulted in the rapid formation of mononitro and dinitro products and sulfur adducts with pyrene and benzo-(a)pyrene.

Hansen et al. (45) presented evidence indicating the possible existence of nitro-PAHs in coal fly ash. Lee et al. (46) reported the presence of dimethyl and monomethyl sulfate in coal fly ash and airborne particulate matter. Although dimethyl sulfate was found at relatively high concentrations (100 ppm) in freshly collected fly ash and plume samples from a coal-fired heating facility without emission controls, no dimethyl sulfate was detected in stack-collected fly ash from a modern coal-fired electric power plant. Monomethyl sulfate was detected in all fly ash samples. Because the collected stack ash samples had been stored for over one year, the authors hypothesized that dimethyl sulfate hydrolyzed to monomethyl sulfate with storage. Therefore, the environmental stability and fate of alkyl sulfates from coal combustion are unknown.

Although chlorinated dioxins have been identified in particles from many combustion sources (47) they have not been identified in coal fly ash samples. In this regard Kimble and Gross (48) failed to detect chlorinated dioxins including 2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD) in fly ash extracts at sensitivities equivalent to less than 2-4 parts per trillion of fly ash. Because of the apparent chemisorption that takes place with organic compounds on fly ash surfaces, adsorbed organic material may not be readily extracted from coal fly ash.

Griest et al. (49) studied the extraction of ^{14}C-labeled PAHs deposited on fly ash surfaces by evaporation of standard solutions. Sonication in benzene resulted in extraction of 26% of the ^{14}C-B(a)P. Extraction efficiency was a function of the number of benzene rings in the PAHs; dotriacontane, napthalene, and phenanthrene were completely recovered, while 90% and 26% of the benz(a)anthracene and benzo-(a)pyrene, respectively, were recovered. Similarly, Mosberg et al. (50) studied the extraction of ^{3}H-1-nitropyrene from fly ash. Admixture of the nitropyrene with fly ash resulted in benzene extraction of 65–90%, while vapor-phase deposition and subsequent extraction resulted in recovery of only 32% of the nitropyrene. Also, incubation in tissue culture media resulted in extraction of 13% of the nitropyrene. Kooke et al. (51) have compared methodology for the extraction of polychlorinated dioxins and furans

from ash derived from municipal incinerators. Generally Soxhlet extraction with benzene or toluene gave the best results; simple shaking or ultrasonic treatment was less efficient.

Biological Evaluation

Mutagenicity Studies

Mutagenicity of extracts of coal fly ash has been described by Chrisp et al. (52). Fly ash mutagens were found to be direct-acting (not requiring enzyme activation) using the Ames Salmonella assay. Thus, the mutagenicity of fly ash cannot be ascribed to the presence of unsubstituted PAHs. Interestingly, extraction of fly ash was performed by incubation with serum. It appears that fly ash mutagens are solubilized by protein binding. Subsequent studies (53) of the same fly ash samples indicated that the finest, most respirable samples were the most mutagenic. However, a 3.2-μm fraction was more mutagenic than the 2.2-μm fraction. A slight, but significant increase in mutagenicity was observed with addition of liver homogenate, indicating the probable presence of small quantities of PAHs. When the fly ash was heated to 350°C, mutagenic activity was no longer detected. Subsequent studies by Hansen et al. (45) indicated that the loss of mutagenic activity with heating was due to decomposition rather than volatilization of fly ash mutagens.

Photostability of fly ash mutagens was demonstrated by irradiation with sunlight, an ultraviolet light, or x-rays. In agreement with the results of Korfmacher et al. (43), it appears that fly ash may stabilize surface-deposited organic mutagens. Comparison of stack-collected ash with ESP-hopper fly ash indicated no detectable mutagenicity in the hopper ash. Similarly, Kubitschek and Venta (54) reported on the absence of bacterial mutagens in hopper ash. It appears that bacterial mutagens are deposited on fly ash surfaces as the flue stream cools and approaches ambient temperatures. Thus, cooling of the exhaust stream may provide a mechanism for inplant capture of fly ash mutagens. Kubitschek and Williams (55) demonstrated that the mutagenicity of fly ash samples (collected from a laboratory-scale combustor) increased during start-up and shut-down. Furthermore, mutagenic activity of fly ash correlated with carbon monoxide content of the flue gas. Thus, it appears that the temperature of combustion and the fuel-air stoichiometry may be critical factors in mutagen production.

Although the direct-acting mutagens in fly ash have not been identified, Hansen et al. (45) have presented data consistent with nitroaromatic hydrocarbons. The solubility of the mutagenic activity in

basic but not acidic aqueous solutions, temperature stability, presence of nitrite in fly ash components, and activity without enzymatic activation are consistent with the expected properties of nitro-PAHs. Application of the techniques recently described by Bjorseth et al. (*56*) should aid in the identification of the mutagenic components in fly ash.

In contrast to the results of bacterial mutagenicity testing, Smith-Sonneborne et al. (*57,58*) have recently demonstrated the presence of temperature-stable fly ash mutagens using the protozoan, *Paramecium tetraurelia*, as the test organism. Furthermore, extraction of the fly ash with dilute HCl but not dimethyl sulfoxide (DMSO) resulted in a significant reduction in mutagenic activity. These results indicate the presence of inorganic mutagens in coal fly ash.

In summary, the mutagenicity of coal fly ash appears to be the result of both organic and inorganic mutagens. The bacterial mutagens appear to be temperature- but not light-sensitive, direct-acting, and present in stack and plume ash samples, but not in ESP-collected material. Further work is necessary to specifically identify the mutagenic components and to evaluate the potential carcinogenicity of coal fly ash.

Toxicity Studies

In vitro toxicity studies have centered on the evaluation of the effects of fly ash on the pulmonary alveolar macrophage (PAM). Garrett et al. (*59,60*) compared the toxicity of particulate samples from coal gasification, fluidized-bed combustion and conventional combustion. They found that the coal fly ash samples were the most toxic to rabbit PAH. Fisher et al. (*61*) compared the PAM toxicity of four-size classified fly ash samples. The finest, most respirable fractions were most toxic; however, the 3.2-μm fraction was more toxic than the 2.2-μm fraction. These results are consistent with the activity of the bacterial mutagens in the same ash samples and indicate that a common process may result in the formation of mutagenic and toxic components in coal fly ash.

Although acute and subchronic inhalation studies have been performed with fly ash, the data derived from these studies are difficult to interpret. Alarie et al. (*62*) and McFarland et al. (*63*) exposed monkeys and rodents to stack-collected fly ash and reported no significant biological effects. However, the aerosols used in the animal exposures had mass median diameters as large as 5.3 μm. Raabe et al. (*64*) exposed Sprague-Dawley rats to reaerosolized ESP ash for 180 days. No significant biological effects were observed. Unfortunately extrapolation of the biological effects from ESP- to stack-collected

fly ash is not possible. Fisher and Wilson (*65*) compared the acute inhalation toxicity of stack-collected fly ash with silica. Although fly ash was found to be as toxic as silica, the biological significance of their results is difficult to interpret because of the use of very high concentrations (125 mg/m^3). Presently there appears to be a deficiency of information on the inhalation toxicology of coal fly ash.

Summary and Conclusions

Collection of representative samples of coal fly ash for physical and chemical analysis and biological evaluation is a major problem area. Although the morphology of coal fly ash particles has been well described, the mechanism of formation of particles is not well understood. Of particular interest with respect to abatement and potential health impact are the physical and chemical factors affecting production of submicrometer particles. Furthermore, the chemical composition of the submicrometer mode requires definition. Elemental analyses of coal fly ash consistently indicate increased concentration of volatile trace elements with decreasing particle size. However, because of the lack of information on the valence state and chemical speciation, little is known concerning biologically availability and potential toxicity. Similarly the bioavailability of the major crystalline components of fly ash, quartz and mullite, is not known. Mullite appears to be encapsulated in an aluminosilicate glass, while quartz may exist as free particles. Laboratory studies have demonstrated organic chemical interactions with fly ash surfaces that can stabilize against or catalyze chemical decomposition. Little is known, however, about the environmental significance of the laboratory studies demonstrating organic chemical interactions with fly ash surfaces. Mutagenic components of fly ash appear to be both organic and inorganic compounds. The bacterial mutagens are direct-acting organic compounds, resistant to photodecomposition, decompose with heating to 350°C and are concentrated in the finest, most respirable fly ash fractions. Because condensation of organic mutagens onto fly ash surfaces predominantly occurs after release to the atmosphere, the mutagenicity of coal effluents is probably underestimated. The protozoan mutagens appear to be inorganic compounds. Neither class of mutagens has been identified, although nitroaromatic hydrocarbons have been implicated. Animal studies employing chronic exposure to realistic fly ash aerosols which simulate human exposure are required.

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